Reaction of (IIb) with PhCoCl. A sample of 0.7 ml (6 mmoles) PhCOCl in 5 ml THF was added to a solution of (IIb) in THF obtained from 1.5 mmoles (Ib) and 3.75 mmoles t-BuOK. After 15 min at −20°C, the mixture was worked up to yield 0.28 g (37%) yellow-orange (VIb)·BF_4, mp 172-174°C (dec., from abs. ethanol). Found, %: 61.42; H 3.90; Fe 11.03. $C_{26}H_{21}$·BF_4FeO_2. Calculated, %: C 61.46; H 4.17, Fe 10.99. PMR spectrum of (VIb)·BR_4: 5.27 s (5H, Cp), 6.54 m (3H, coord. Ph), 6.80 d (2H, coord. Ph), 7.29 s (1H, CH), 7.49 m (3H, uncoord. Ph), 7.66 m (2H, uncoord. Ph), 7.78 m (3H, uncoord. Ph), 8.27 d (2H, uncoord. Ph). IR spectrum: ν(CO) 17.40, $\nu(BF_\alpha)$ 1040-1080 cm^{-1}.

CONCLUSION

1. α-Deprotonation was carried out for the first time for arene-Cp-ruthenium compounds.

2. The reactions of the deprotonation products with electrophiles Me_3SiCl, MeI and PhCOCl were studied.

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OXIDATION OF MESITYLENE BY $PtCl_6^{2-}$ IONS IN TRIFLUOROACETIC ACID

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Heating of a solution of an aromatic compound and $PtCl_6^{2-}$ ions in acetic acid or aqueous CF_3CO_2H leads to the formation of σ-aryl Pt(IV) complexes. The platinum atom enters only the meta and para positions relative to the substituent [1, 2]. σ-Complexes are not formed in reactions with such hydrocarbons as p-xylene, mesitylene and pentamethylbenzene. However, an oxidation–reduction reaction of Pt(IV) ions with hydrocarbon proceeds giving a Pt(II) complex not containing organic ligands. In the present work, we studied this reaction for mesitylene (MS).

Heating of a solution of H_2PtCl_6 and MS in aqueous CF_3CO_2H at reflux gives a single organic product, namely, (2,4,6,3',5'-pentamethyl)diphenylmethane (I) in 60% yield

$$2\,1,3,5\text{-}C_6H_3(CH_3)_3 + PtCl_6^{2-} \longrightarrow [3,5\text{-}C_6H_3(CH_3)_2]CH_2\,[2,4,6\text{-}C_6H_2(CH_3)_3] + PtCl_4^{2-}$$

(I)

The kinetic curves for the loss of $PtCl_6^{2-}$ ions and accumulation of (I) are given in Fig. 1. The drop in the $PtCl_6^{2-}$ concentration was followed for 40 min when the solution became nonhomogeneous due to the formation of Pt(II) derivatives with poor solubility. The accumulation of (I) was linear. Bubbling of oxygen through the solution leads to a more rapid formation of (I) at the onset; the concentration of this product remains virtually invariant subsequently. The oxidation coupling of monosubstituted arenes to diaryls by the action of $PtCl_6^{2-}$ ions proceeds with the intermediate participation of a σ-aryl Pt(IV) complex [3]. In the case of MS, the intermediate generation of such a complex is excluded because of steric factors. Thus, the most likely mechanism for the formation of diarylmethane from MS is the one-electron oxidation of the arene to a radical-cation, which may be readily converted to a substituted benzyl radical capable of attacking a free MS molecule. Oxidation of the intermediate by the Pt complex or O_2 gives diarylmethane (I).

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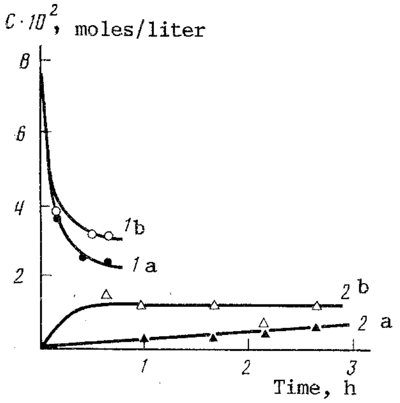

Fig. 1. Consumption of $PtCl_6^{2-}$ ions (1) and accumulation of (I) (2) in the oxidation of mesitylene (1.23 mole/liter) in 4.5:1 CF_3CO_2H–H_2O at 84°C in the absence of oxygen (a) and with oxygen bubbling (b).

It is not excluded that the first step in the reaction of $PtCl_6^{2-}$ ions with sterically hindered arenes is also a one-electron transfer. In this case, the second step is a recombination of radical species, namely, the arene radical-cation and Pt(III) complex, with the formation of a Wheland complex. Such a recombination of the MS radical-cation and the Pt(III) species is apparently impossible and reaction subsequently proceeds by a different mechanism. Analogous behavior was observed upon the oxidation of polymethylbenzenes by a Pd(II) complex in CF_3CO_2H [4] and the formation of an arene radical-cation was detected by ESR spectroscopy for this system. The participation of a radical pair is proposed in the first step of the reaction of $PtCl_6^{2-}$ ions with arenes stimulated by light irradiation [2, 5].

An alternative mechanism for the generation of a substituted benzyl radical (or carbocation) from MS may be cleavage of a C—H bond in the CH_3 group with the formation of a σ-alkyl Pt(IV) complex (an analogous σ-methyl complex was detected in the reaction of $PtCl_6^{2-}$ ions with methane [6]). The benzyl radical in this case may be obtained in the homolysis of the Pt—C bond as proposed for σ-aryl complexes [3]. However, σ-alkyl Pt(IV) complexes readily react with water [7] and, thus, we might expect the corresponding benzyl alcohol in significant amounts among the reaction products.

EXPERIMENTAL

2,4,6,3',5'-Pentamethyldiphenylmethane (I). A solution of 1 g $H_2PtCl_6 \cdot 6H_2O$, 2 ml mesitylene and 3 ml water in 12 ml CF_3CO_2H was heated at reflux for 3.5 h. The solvent was evaporated at reduced pressure to 2 ml and 10 ml water was added to the residue, which was extracted thrice with chloroform. The extracts were combined, washed with water and dried over Na_2SO_4. Chloroform was evaporated at reduced pressure. The residue was subjected to thin-layer chromatography on silica gel with hexane as eluant gave 0.19 g (60%) (I), mp 66-67°C [8]. PMR spectrum (δ, ppm, $CDCl_3$): 6.81 s (2H, phenyl), 6.76 s (1H, phenyl), 6.57 s (2H, phenyl), 3.89 s (CH_2), 2.22 (CH_3), 2.18 s (CH_3).

Under similar conditions, the reaction was carried out by bubbling O_2 over the solution. Using this method, the yield of (I) was 76.%.

CONCLUSION

The reaction of $PtCl_6^{2-}$ ions with mesitylene in aqueous CF_3CO_2H leads to the formation of 2,4,6,3',5'-pentamethyl)diphenylmethane.

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